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PHASE DIFFERENTIATION AND CHARACTERIZATION OF NANOSTRUCTURED COMPOSITES BY SYNCHROTRON RADIATION TECHNIQUES

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Abstract

The complexity of nanostructured materials presents challenging difficulties in characterization using conventional techniques. For example, conventional x-ray diffraction may not provide accurate information on the structure (solid solution or phase separation) of nanostructured materials. Complementary advanced characterization methods are often required in the detailed understanding of structures. In this paper we report our work on characterization of two nanostructured systems, namely, AgNi powder and NiCo films, using synchrotron radiation techniques of x-ray diffraction, anomalous x-ray scattering and x-ray absorption spectroscopy.

1. Introduction

Structural characterization of alloys by conventional x-ray diffraction (XRD) has been well established [1]. For materials with coarse grain size, the appearance of a single set of diffraction peaks and the disappearance of elemental peaks are commonly accepted as evidence of formation of an alloy. In a random, substitutional solid solution, the lattice parameter changes with composition and the variation can be qualitatively followed using Vegard's law. When the crystallite size (or x-ray coherence length) of a material is decreased to below a certain critical length scale, a nanostructured solid solution cannot be unequivocally determined from a composite using conventional x-ray diffraction [2]. In a nanocomposite where the two phases have close lattice parameters and x-ray structural coherence, the Bragg peak of one phase has some degree of overlap with that of the other phase. Because of the effects of size broadening and the contribution to diffraction amplitude by structural coherence of the two phases, a single peak will appear for a particular Bragg reflection when the size is below a certain limit. However, this single peak has an average lattice spacing that has no correspondence in real space, and can be easily mistaken as evidence of formation of an alloy. Therefore, conventional XRD, used for probing long-range ordered atomic structure, should not be used alone to study the structure of nanostructured alloys and composites made of structurally coherent and immiscible materials. Instead, other tools, or more often a vast combination of different techniques, which do not suffer from such limitations should be considered.

The structural characterization of nanostructured metastable alloys, prepared by non-equilibrium processing such as mechanical alloying and vapor quenching, has already required the use of techniques other than conventional XRD. For example, techniques such as Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) and solid-state nuclear magnetic resonance spectroscopy (NMR) were used to investigate the average local atomic environment of Co-Cu, in order to confirm if the nanostructured material was a solid solution or a composite [3]. Both techniques rely on the use of suitable reference standard materials for comparison. However, in certain composites where the elements have very similar scattering potentials, such as Ni-Co, EXAFS cannot be used to separate the scattering effects from different elements and the advantage of being an element-specific structural analysis tool is greatly reduced. Further, since the primary EXAFS signal is given rise by the short-range order of the sample, one will not be able to separate different phases of different long-range order coexisting in the composite.

Diffraction anomalous fine structure (DAFS)[4,5], a technique combining diffraction and XAS (X-ray Absorption Spectroscopy, a general term covering EXAFS and XANES), can be used to selectively provide short-range order information of the long-range ordered atoms associated with a particular Bragg reflection, and the information on specific chemical valence at inequivalent atomic site. The spatial selectivity can be used to study the local atomic structure of multiple-phase materials, when the phases in the sample give rise to diffraction peaks at different locations. In the case of a random,

homogeneous, nanostructured alloy, x-ray absorption spectra should display the characteristic of the constituent elements of each phase as well as their binding and local structure associated with the Bragg peaks. However, in the case of nanostructured alloy, the diffraction peaks are rather weak and broad and therefore hamper the generation of a detailed radial distribution function by the standard Fourier transform due to the low signal intensity. Nevertheless, the elemental information can be easily obtained by the similar method, anomalous x-ray scattering (AXS), and yields information on the formation of solid solution. In this article, we report the structural investigation of nanostructured Ag_xNi_{1-x} powders and Ni_xCo_{100-x} films, using synchrotron radiation techniques of x-ray diffraction, anomalous x-ray scattering and X-ray absorption.

2. Experimental

Nanocrystalline $Ag_{1-x}Ni_x$ (x=0.2-0.8)[6] powders were prepared by the gas condensation method [7]. The deposition chamber was first evacuated to $\leq 1x10^{-5}$ Torr and then back-filled with helium of ~2 Torr before metal evaporation. Pure Ag and Ni were co-evaporated by resistive heating from a tungsten boat. Following rapid evaporation of the metals, small particles formed by condensation from Ag and Ni atoms in helium. They were then transported via the convection of helium gas and deposited on a liquid nitrogen cooled trap. The distance between the cold trap and the evaporation source was approximately 4 cm. Such distance was optimized to ensure that the smallest nanocrystalline particles were synthesized. The evaporation and condensation typically occurred in a very short time. The compositions of powders were controlled by using different evaporation source contents.

As-synthesized powders were examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). A Rigaku D/MAX IIIA θ-2θ diffractometer with filtered Cu K_α radiation (wavelength = 1.5406 Å) was used in conjunction with a graphite monochromator. The diffraction profiles were analyzed quantitatively using a profile fitting program to obtain accurate peak position and full-width at half-maximum (FWHM) values. Line broadening was used to estimate the average crystallite size whenever such analysis is possible. Under conditions optimized for the synthesis of the finest particles, an average particle size range of 5-20nm was obtained in these samples. High-resolution TEM (HRTEM) (JOEL 2010F) with electron diffraction capability confirmed the nanocrystalline nature of these materials. Synchrotron radiation experiments were conducted at two third-generation synchrotron facilities: Synchrotron Radiation Research Center (SRRC), Taiwan and the Pohang Light Source (PLS), Korea. EXAFS measurements were performed at B11-DCM beamline, (SRRC) and 3C1 beamline (PLS) using both fluorescence and transmission modes of detection. Soft-x-ray XAS and photoemission spectroscopy experiments were carried out in the 6m-HSGM (High energy Spherical Grating Monochromator) beamline (SRRC) in an ultrahigh vacuum chamber.

The Ni_xCo_{100-x} magnetic films were deposited on Cu substrates using the non-aqueous electroless method known as the Polyol [8]. It involved the reduction and deposition of constituent atoms in refluxing ethylene glycol at 194 °C. The films with

compositions of Ni_{100}, Co_{100}, $Ni_{90}Co_{10}$ and $Ni_{50}Co_{50}$ were studied using conventional XRD and synchrotron techniques of EXAFS and anomalous x-ray scattering. The study was carried out at beamlines DB-11 of SRRC and 5C2 at PLS. Anomalous x-ray scattering (AXS) provided site-selective, structural information of nanostructured films that could not be obtained by either XRD or EXAFS alone, or combined.

3. Results and discussion

3.1 AgNi nanocomposite powders

According to the phase diagram of binary alloys, solid solutions of AgNi cannot be formed [9]. The solid solubility of Ni in Ag is as low as 0.1% even at 750 °C. Several efforts to produce such a solid solution by creating metastable states under extreme conditions, such as liquid quenching, did not lead to a reproducible fabrication procedure. The formation of the solid solution was only reported on thin films using laser ablation deposition [10,11], co-evaporation method [12], and recently mechanical alloying [13]. Taking advantage of the high surface-to-bulk energy ratio, which is characteristic of nanocrystals, we were able to prepare samples [7] containing significant amounts of AgNi alloy phase with a wide range of compositions using a co-evaporation of Ag and Ni.

As-synthesized nanocrystals had average particle size of 5-20nm as examined by TEM [7]. Three types of X-ray absorption spectra were measured: X-ray Absorption Near Edge Spectroscopy (XANES), Extended X-ray Absorption Fine Structure (EXAFS) and soft-X-ray absorption spectroscopy, to investigate the electronic properties, the local structure and the stability of the AgNi binary alloys. Photoemission spectroscopy was used to identify the chemically different species. Our results indicate that, by controlling the processing parameters and therefore varying the particle size, materials with new properties can be obtained which can be potentially important for industrial applications such as catalysis, magnetic recording and sensor technology.

Note that XAS has a rather large probing length and this property can eliminate or at least reduce contributions from the complicated surface properties of nanoparticles, which dominate several other more surface sensitive spectroscopy techniques. Specifically, the probing length of the XAS (even by total electron yield (TEY) detection) is longer than 5 nm. This matches well with the average particle size of our samples, thus enabling us to perform "bulk" measurement.

(a) Intensity (Arbitary Units)

Ag (111)
Ag(200)/Ni(111) $Ag_{1-x}Ni_x$
Ni(200)

X=0.8
X=0.65
X=0.5
X=0.35
X=0.2

20 40 60 80 100 120 140

(b) Intensity (Arbitary Units)

$Ag_{1-x}Ni_x$
Heat Treated
Ni(200)

X=0.8
X=0.65
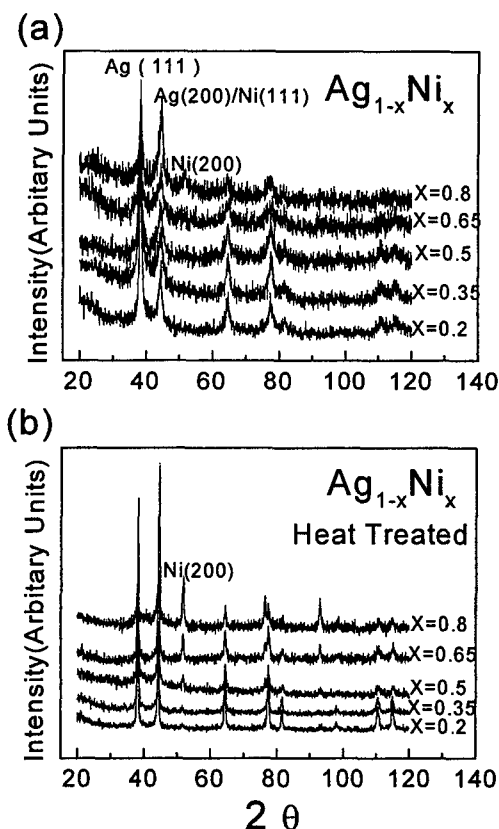X=0.5
X=0.35
X=0.2

20 40 60 80 100 120 140

2 θ

Fig. 1 - X-ray powder diffraction of the AgNi nanocrystals with different compositions. (a) as grown sample (b) after heat treatment.

The first evidence of the formation of an AgNi solid solution was suggested by the absence of the Ni (200) XRD peak in as-synthesized samples. As shown in Fig. 1(a), Ni (200) is barely visible in the sample of high Ni concentration. The measured Ni K edge absorption intensities remain nearly proportional to the Ni contents in these samples. The nearest neighbor bond lengths, 2.1-2.5 Å with a nearly linear relation with respect to the Ni composition, deduced from the Ni K EXAFS oscillations, are shown in Fig. 2(a). Similar to the Vegard's law commonly used to deduce the alloy composition from the lattice parameter [1] obtained by XRD, such a relation indicates the formation of the AgNi solid solution. The disappearance of the Ni (200) diffraction peak in the mixed Ag-Ni phase, therefore, can only be attributed to the loss of long-range order of Ni in the formation of solid solution.
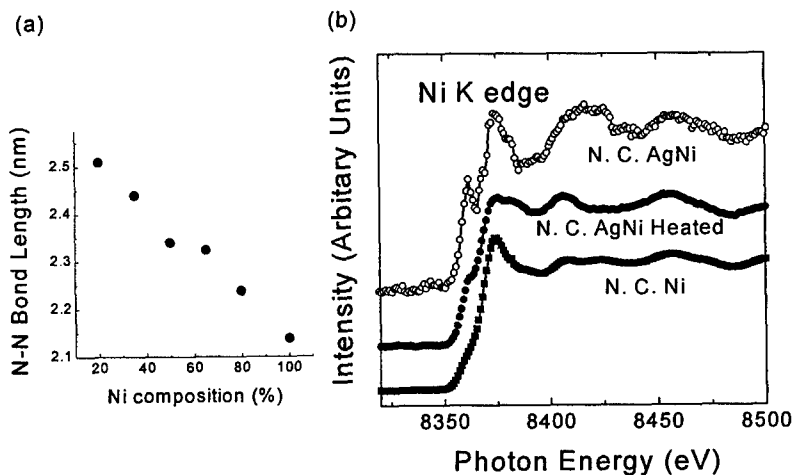
(a)

(b)

Fig. 2 - (a) The nearest-neighbor bond length deduced form the Ni K edge spectra of $Ag_{1-x}Ni_x$ (x=0.2-0.8). (b) Ni K absorption spectra of AgNi nanocrystals before and after high temperature annealing. The spectra are compared with commercial Ni nanocrystalline powders (bottom curve).

A similar behavior can also be expected in the case of Ag although Ag (111) and (200) diffraction peaks were observed. The widths of the Ag diffraction peaks reveal, in fact, that the corresponding domains are much larger than the average particle size of our AgNi nanocrystals. Therefore, we can conclude that the measured Ag (111) and (200) diffraction peaks are a result of Ag that did not participate in the mixing process. Such type of inhomogeneous morphology has also been imaged with HRTEM measurement of our samples. The inhomogeneous size distribution of Ag indeed created much more difficulties in the precise determination of the microstructure. For example, the EXAFS measurements of the Ag L absorption edge with different compositions show almost no difference, which can be again attributed to that the larger Ag particles did not participate in the formation of solid solution. They dominated the EXAFS spectra since they had higher order.

The sharp feature in the edge region — see the top spectrum in Fig 2(b) — at a photon energy of approximately 8365 eV is another strong indication that the Ni atoms of our samples are in a very different electronic structure than those of commercial Ni powders which are also in a nanocrystalline form. Samples prepared with different noble gas pressure, which usually leads to different particle sizes, do not exhibit strong differences in the X-ray absorption spectra. However, the subsequent heat treatment caused drastic changes in the near-edge region and the EXAFS region. Note the

sintering of the sample is conducted on pellets of compacts powders. It is concluded that as-prepared AgNi nanocrystals were metastable alloys and heat treatment to > 320 °C caused the phase separation of the elements.

The drastic decrease of the Ni $L_{2,3}$ absorption spectra intensity of the nanocrystalline AgNi pellets upon heating (not shown here)[14] indicates that a strong segregation of Ag and Ni occurred at the temperature above 320 °C. Since the free energies of Ag and Ni increase with temperature and become eventually larger than the free energy gained by alloying in the nanocrystals, the segregation becomes energetically favorable above a certain temperature. We also observed the dependence of phase segregation on particle size (the relative AgNi solid solution content) in samples upon heating. For samples with particle size of 50 nm and larger (under different control parameter and not included in the discussion of this work), the gain in the surface energy is not enough to form substantial amount of AgNi solid solution and, therefore, no segregation can be detected.

A simple empirical rule can be used to examine the surface segregation of transition metal alloys: the constituent with lower elemental surface tension enriches the alloy surface [15]. The same argument leads to a surface enrichment of Ag since the surface tension of the Ag in the liquid phase is lower than that of Ni [16]. The segregation temperature measured in our present experiment is consistent, within the accuracy of our temperature measurement, with that derived from the temperature dependent X-ray powder diffraction measurements. The result of the X-ray diffraction of the sample after heating to above 420 °C followed by a rapid quenching shows Ni(200) (Fig. 1b). Scanning electron microscopy (SEM) micrographs showed a sharp segregation between Ag and Ni, with Ni buried under Ag in a thin film-like arrangement. The segregation explains the decrease in the Ni L absorption signal.

In order to clarify the causes of alloying, we simulated the process by depositing Ni on Ag clusters prepared on HOPG (Highly Oriented Pyrolitic Graphite), SiO_2 surfaces (natural oxide of Si (100) wafer) and on TiO_2 nanocrystalline particles [17]. It is well known that small amounts of Ag on HOPG and SiO_2 form clusters with small size [18]. In our case, only ~0.05 monolayer (ML)(nominal) of Ag was deposited first and Ni was then deposited at room temperature with increasing coverage. Synchrotron photoemission spectroscopy was used to detect possible alloying or chemical reactions. Both valence and core level spectra were collected and their spectral intensities are also used as a quantitative indication of the metal deposition. Typical valence band spectra in such sequence are shown in Fig. 3(a) on which Ag and Ni were deposited on sample substrate, a Ta foil, covered with TiO_2 nanocrystals.

We did not find any evidence of Ag-Ni bonding or atomic exchange on the Ni/Ag covered HOPG and SiO_2 surfaces by examining both valence and core level spectra. However, in the case of deposition on the TiO_2 nanocrystalline particle surfaces, the Ag $3d$ core level spectrum, shown in Fig. 3(b), exhibits a clear shoulder on the low-binding energy side, compared to the Ag 3d spectrum taken on the freshly deposited Ag. The amount of Ni deposited here was approximately 0.03 ML, a small amount not yet sufficient to metallize the surface. Based on the valence band spectra in Fig. 3(a), more than 0.1 ML of Ni is needed to produce spectral intensity at the Fermi level, indicating the metallized surface is metallized. In this case, the shoulder appearing on the low-
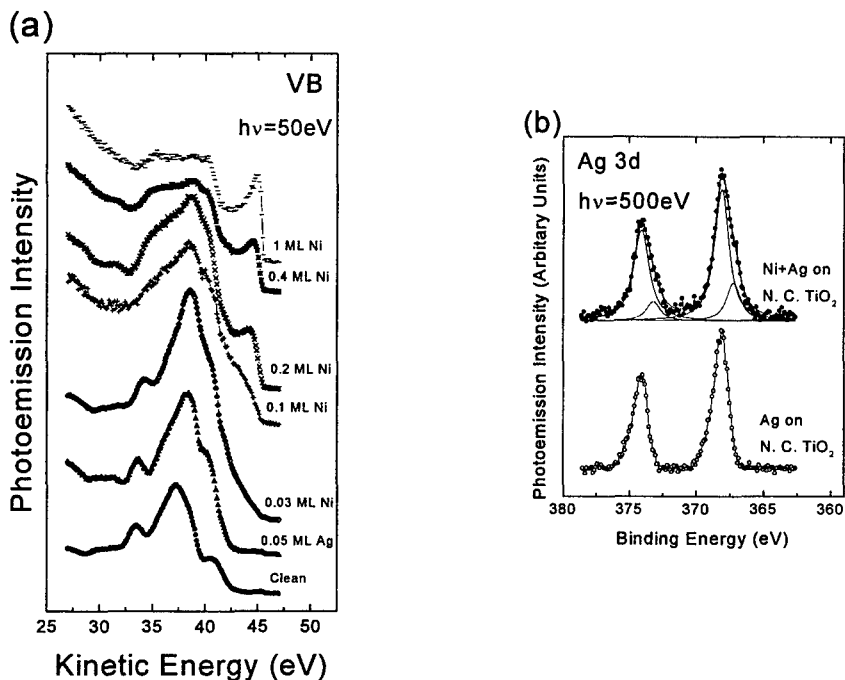
(a)

(b)

Fig. 3 – (a) Valence band photoemission spectra of the metal deposition sequence taken at a photon energy of 50 eV. The substrate is TiO_2 covered Ta foil. (b)Photoemission Ag $3d$ core level spectra taken at a photon energy of 500 eV. New components are developed on the low binding energy side of the spectrum of Ag nanocrystals (deposited on TiO_2) covered with Ni. Spectrum with open circles is taken with Ag nanocrystals.

binding energy side of the spectrum is not likely due to local charging related to the partial metal coverage. Instead, it indicates the existence of a new phase of AgNi similar to what was observed in the nanocrystalline samples grown by gas evaporation.

Subsequent XANES measurements on the Ni K edge on these samples also confirms this phase by giving rise to a similar near edge structure. The particle size of AgNi grown on TiO_2 is as small as the AgNi nanocrystalline particles grown by the gas evaporation method. Ag and Ni grown on the HOPG and SiO_2 apparently have much larger particle size, approximately 500 nm, according to SEM micrographs. This difference in the particle size again is consistent with the spectroscopy measurements. Thus, it is likely that the major driving force for the AgNi alloy formation is the high surface energy of nanocrystals. The only apparent role of the growth kinetics during the gas evaporation process is on small particle size.

In summary, X-ray diffraction and EXAFS measurements revealed the existence of the solid solution phase by the disappearance of Ni(200) diffraction peaks and by the linear relation of the Ni nearest neighbor bond length with respect to the Ni composition. The new feature in the XANES spectra further indicates that the AgNi solid solution is formed.

The alloy is stable from room temperature up to 320 °C. Heating the pellet samples above 320°C causes Ag and Ni to segregate and thin films of Ag and Ni are formed with Ag on top of Ni. The near edge spectra of heat-treated samples are much closer to bulk Ag and Ni than before heat treatment. An effort to simulate the gas evaporation process with a procedure under ultrahigh vacuum failed to yield similar alloy particles on the HOPG and SiO_2 surface. On the other hand, Ni and Ag deposited on TiO_2 give rise to a new component on the low-binding-energy side of the Ag $3d$ spectrum which can be explained by the formation of an AgNi alloy. This indicates that the surface energy plays the key role in allowing the production of the new alloy.

3.2 NiCo nanocomposite films [19]

Nickel and cobalt have mutual solubility at equilibrium. The lattice parameters for fcc Ni and fcc Co are 3.5238 Å and 3.5447 Å, respectively. The K absorption edges for Co and Ni are 7.709 keV and 8.333 keV, respectively. Although EXAFS has been widely accepted as a very useful tool to study nanostructured metastable alloys, it is not suitable for investigating materials consisted of elements (such as Ni and Co) with very close lattice parameters, backscattering amplitudes and phase shifts. Therefore, the EXAFS results of the Ni edge and Co edge of $Ni_{50}Co_{50}$ and $Ni_{90}Co_{10}$ (not shown here) did not show noticeable difference from the elemental films. The EXAFS data were therefore inconclusive regarding the mixing of these elements in the films.
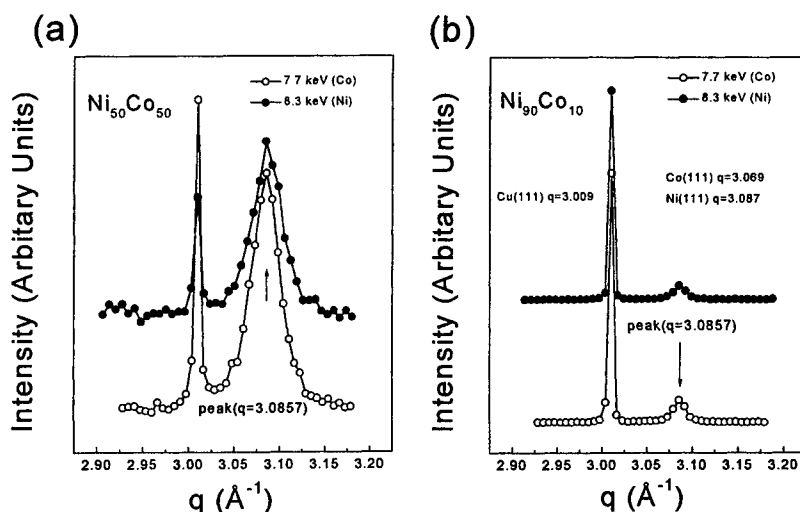

Fig. 4 - XRD powder scans of (a) $Ni_{50}Co_{50}$ and (b) $Ni_{90}Co_{10}$.
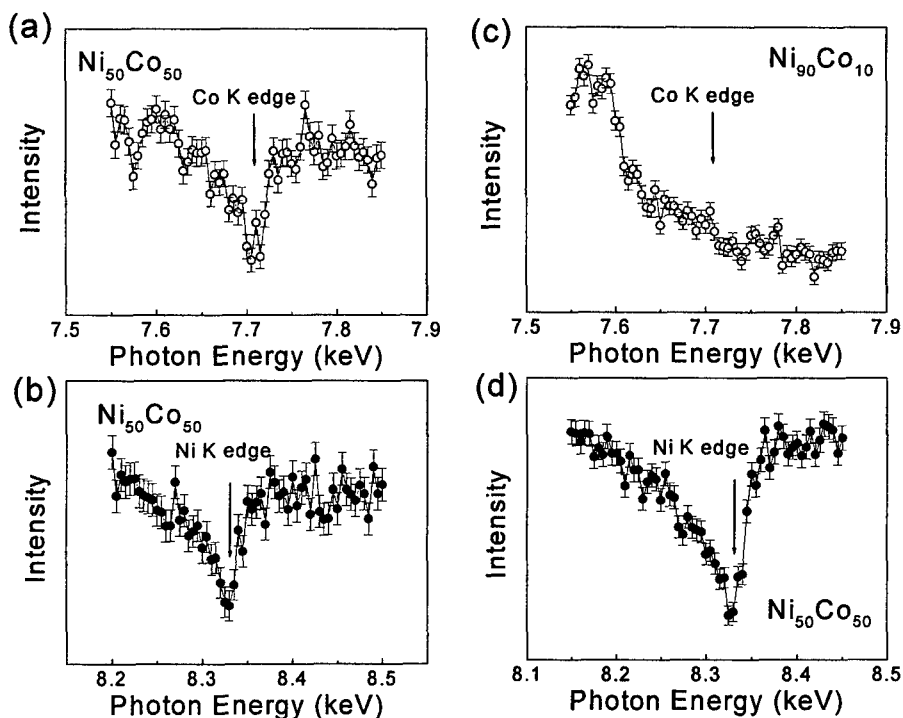
Fig. 5 - AXS results of the XRD peak at q=3.085 Å^{-1} of (a) $Ni_{50}Co_{50}$ scanning across Co, (b) Ni absorption edges, and (c) of $Ni_{90}Co_{10}$ scanning across Co and (d) Ni absorption edges.

Conventional XRD results showed these films were polycrystalline and had a single set of fcc diffraction peaks without any sign of elemental separation. Because of the close lattice parameters of fcc Ni and fcc Co, the formation of alloy or composite could not be ascertained, as also reported for $Ni_{80}Co_{20}$ powders synthesized using similar method [20]. The average crystallite size of Ni_{100}, Co_{100}, $Ni_{90}Co_{10}$ and $Ni_{50}Co_{50}$ was in the range of 15 to 64 nm. For anomalous x-ray scattering measurements, powder diffraction experiments were first performed to determine the position of the (111) Bragg reflection of the films (q = 3.086 Å^{-1}) at each photon energy. The powder scans of $Ni_{50}Co_{50}$ and $Ni_{90}Co_{10}$ are shown in Figs. 4(a) and 4(b). Only a single peak at the (111) reflection existed in these films. The momentum transfer was fixed to the (111) reflection of the film, i.e. q = 3.086 Å^{-1}, and the scattering intensity was monitored as the x-ray energy was varied through Ni and Co absorption edges, respectively.

If the element in question is related to the specified Bragg peak, then the elemental absorption causes a decrease in the Bragg intensity at its absorption edge. A cusp, caused by the interference between the Thomson scattering amplitude and the real part

of the anomalous scattering amplitude [4], is observed in the energy scan of the Bragg peak. Such behavior was observed for the Ni_{100} and Co_{100} films.

Figure 5 shows the AXS measurement of the (111) peaks of $Ni_{50}Co_{50}$ and $Ni_{90}Co_{10}$. Both Ni and Co were related to this Bragg peak for $Ni_{50}Co_{50}$. For $Ni_{90}Co_{10}$, only Ni was found in this Bragg peak. However Co absorption was absent. It is noted that EXAFS and energy dispersive analysis confirmed the existence of Co in this sample. Thus, within our detection limit of AXS, Co was not associated with the (111) Bragg peak of this film. Only Ni solely contributed to this long-range order. The detection limit of long range order using XRD is roughly 3 nm. The absence of Co in the (111) Bragg peak of $Ni_{90}Co_{10}$ suggested that Co did not alloy with Ni in this atomic arrangement. Further AXS work using other Bragg peaks of the films is in progress to investigate if Co was associated with other peaks or amorphous.

In summary, for AgNi nanocomposite powders, EXAFS, XANES, soft-x-ray and photoemission spectroscopy were used to identify the miscible phase and its most likely origin. For NiCo nanocomposite films, AXS technique was added to this approach in order to gain more specific information on the alloy formation. It is clear, regardless of the apparent success, that further work needs to be performed on exploiting the AXS technique with more sophisticated peak fitting and simulation, as well as on improving the resolution limit.

Acknowledgment

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